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EP-A-0 023 095  
DE-A-2 718 594  
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US-A-3 698 878

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TABLE I

5	Composition designation units	Binder matrix wt percent	Hardness Rockwell A	Abrasion resistance l/volume loss cm <sup>3</sup>	Transverse rupture daN/mm <sup>2</sup>	Fracture toughness (K <sub>IC</sub> ) daN.mm <sup>-3/2</sup>
	X7503-86	20% Ni; 1.2% C; Fe*	87.5	5.0	275.76	45.14
10	X7503-86A	20% Ni; 0.9% C; Fe*	87.5	4.0	275.76	52.08
	X7503-86B	30% Ni; 0.9% C; Fe*	87.0	3.5	258.52	58.34
15	X7503-86E	30% Ni; 0.5% C; Fe*	85.4	2.1	289.54	60.07
	X7503-86F	40% Ni; 0.5% C; Fe*	85.4	2.1	296.44	63.20
	X7503-86G	50% Ni; Fe*	85.0	1.8	303.33	59.03
20	X7503-86H	40% Ni; Fe*	86.2	1.9	248.18	55.56
	X7503-86J**	30% Ni; 0.5% C; Fe*	87.0	3.3	289.54	61.11
25	Grade 55B	100% Co	86.7	2.5	289.54	54.86
	Grade 268	100% Co	87.3	2.8	337.80	50.35

\* balance to 100%

30 \*\* X7503-86J uses a finer WC particle size than its otherwise identical composition (X7503-86E).

Compositions X7503-86 and X7503-86A had relatively low nickel additions and relatively high carbon additions. These compositions had a fracture toughness (K<sub>IC</sub>) which was inferior to that of comparable commercial grade WC-Co. i.e., Grade 55B and Grade 268.

35 Compositions X7503-86B, X7503-86E, X7503-86F and X7503-86J, in which the nickel addition was from 30 to 40% and the carbon addition was 0.5%, showed a substantial increase in fracture toughness without significant decrease in abrasion resistance.

40 Compositions X7503-86G and X7503-86H, in which the nickel addition was in excess of 40% and the carbon was eliminated showed fracture toughness and abrasion resistance which were lower. Because abrasion resistance is equally as important as is fracture toughness to suitability of compositions for rock drilling, these compositions, even though equal or superior to commercial Grades 55B and 268 in fracture toughness, were inferior.

#### 45 Example II

Tungsten carbide sample compositions, all consisting of 88% by weight of tungsten carbide and 12% by weight of binder matrix were prepared. Their physical properties were determined and were compared with designated standard commercial grades of WC-Co compositions, as follows:

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The metallic alloy comprises and may consist of from about 5 to about 50% by weight nickel with the remainder or balance being iron apart from impurities. Within the foregoing proportions, such alloys may provide substantial improvement of, in particular, the critical property of fracture toughness.

In addition to the foregoing metallic components and at expenses of the balance component, the alloy should contain a sufficient amount of carbon to avoid the formation of carbon deficient phases. Generally, no more than about 2% carbon by alloy weight will be present. An excess of carbon, sufficient to produce a C-2 or above rating per ASTM specification B-276 should be avoided also. Such an excess may reduce the desirable performance characteristic of the composition.

This carbon performs several functions in the alloy. Most importantly, it may be utilized to avoid the formation of harmful double carbides of, for example, iron with the tungsten. Such double carbides are generally quite brittle and therefore also detract from important properties of the composition.

In a further embodiment of the present invention, the alloy of the binder matrix additionally contains manganese, desirably from about 5 to about 20% by weight. This metal component has been discovered to be especially advantageous in the foregoing alloys where they contain about 5 to about 30% by weight nickel.

The present cemented carbide compositions may be employed in any necessary shape and prepared by standard cemented carbide manufacturing techniques. For convenience, the separate alloy components (generally in finely powdered form) are first mixed together, for example in a ball mill. The admixture may then simply be pressed or molded into the desired shape. These steps are usually performed in the presence of a lubricant such as paraffin or polyethylene glycol which can subsequently be substantially removed.

Once in (or simultaneous with formation of) the desired shape, the molded components can be sintered by any standard carbide sintering technique known to one skilled in the art. Upon cooling, this yields an integral compact suitable for initial use.

For those compositions containing manganese, it is preferred to heat them in hydrogen or other reducing gas to the liquidus temperature of the binder and then complete the sintering in an inert or reducing gas. This is done to keep the loss of manganese from the composition to a minimum.

Many of the unique and desirable properties of the present invention are believed to arise from a strain-induced partial transformation of the austenitic matrix alloy to martensite. This occurs under a variety of circumstances, including high applied stress. In the case of Hertzian contact (similar to that experienced by compacts in rock drilling) the surface layer will partially transform to martensite while the interior portion will remain austenite.

In accordance with the present invention, strain-induced transformation is believed to cause the present composition to exhibit a hardened surface, which enhances the wear resistance, while retaining a tough core of austenitic alloy matrix to resist breaking. The requisite cold working (or strain hardening) for the partial alloy transformation will take place under the conditions of use of the cemented carbide composition in, for example, rock drilling.

The presence of manganese in the subject alloys has an especially significant effect on this phenomenon. The manganese provides a highly desirable hardening transformation when the matrix binder is subjected to plastic deformation, such as that resulting from high applied stress. Work hardening is localized at the outer surface region of the composition, where the stress is applied. Consequently, the overall toughness of the product is maintained.

The invention of this application will be more fully described and better understood from the following examples and comparative results.

#### Example I

Various tungsten carbide sample compositions were prepared containing from 84 to 85% by weight of tungsten carbide and 15 to 16% by weight of binder matrix. These samples contained differing alloy constituents. Their physical properties were determined and were compared with the standard commercial grades of tungsten carbide—cobalt binder (WC-Co). as follows:

TABLE II

Compositions designation units	Binder matrix components		Hardness Rockwell A	Abrasion resistance l/vol. loss (cm <sup>3</sup> )	Fracture toughness (K <sub>IC</sub> ) daN.mm <sup>-3/2</sup>
	Amount	wt. percent			
X7801-301	12%	20% Ni; 10% Mn; 1.5% C; Fe*	85.7	5.5	59.03
X7800-302	12%	25% Ni; 10% Mn; 1.5% C; Fe*	85.5	4.3	62.50
Grade 231	10%	100% Co	87.7	3.6	52.08
Grade 55B	16%	100% Co	86.7	2.5	54.86

\* balance

All compositions of this invention showed significant improvement in abrasive resistance and fracture toughness. Thus the combination of properties exhibited by those compositions having iron/nickel/manganese/carbon alloy binders were particularly desirable are shown in Figure 2.

#### Example III

A hardness profile was determined on inserts used for drilling rock for each of the following:

Designation	Binder matrix	
	Amount	Components
X7800-302G	12%	25% Ni; 10% Mn; 1.5% C, Balance Fe
X7800-301Aa	12%	20% Ni; 10% Mn; 1.5% C, Balance Fe
Grade 231	10%	100% Co
Grade 55B	16%	100% Co
Grade 241	10%	100% Co

These profiles were obtained by Tukon Microhardness tester using a knoop indenter and a 500 gram load. They are plotted as the graph of Figure 1.

As depicted in Figure 1, both samples of the present invention show bases for their substantial improvement over standard grades of cobalt-bound compositions. At the composition surfaces, samples X7800-302G and X7800-301Aa exhibited the highest degree of work hardening. This localized surface superiority translated directly into improved wear resistance, particularly under high applied stress.

That surface superiority was combined with a rapid and substantial decrease in hardness with distance from the compositions surface. Thus, they also displayed higher degree of localization of hardness superiority. This in turn permits the retention of internal toughness. Consequently, the compositions of the present invention exhibited relatively higher overall toughness than ones bound with a conventional cobalt matrix.

Figure 2 also shows the superiority of various of the present compositions. There the relative fracture toughness and abrasion resistance for the sample and commercial compositions of Example II are depicted. It may be seen from Fig. 2 that the properties of the present compositions are superior to those of conventional tungsten carbide-cobalt ones.

#### Claims

1. A cemented composite comprising refractory particles comprising tungsten carbide and, optionally, additions of titanium carbide, tantalum carbide and/or other refractories within a metallic matrix binder, wherein said matrix represents between 3 and 20% by weight of said composite and consists of between 5 and 50% nickel, an amount of up to 2% carbon sufficient to avoid formation of detrimental carbon deficient or excess phases and the balance consisting of iron apart from impurities.

2. A cemented composite comprising refractory particles comprising tungsten carbide and, optionally, additions of titanium carbide, tantalum carbide and/or other refractories within a metallic matrix binder, wherein said matrix represents between 3 and 20% by weight of said composite and consists of about 5 to about 30% nickel, 5 to 20% manganese, an amount of up to 2% carbon sufficient to avoid formation of detrimental carbon deficient or excess phases and the balance consisting of iron apart from impurities.
3. The composite of claim 1 or 2 wherein the composite has an austenitic matrix which partially transforms to martensite at the surface under applied stress.
4. A process for drilling through rock with a cemented carbide tool, wherein said tool is composed of the cemented carbide composite of any one of the preceding claims.
5. A process for producing the composite of any one of claims 1 to 3 comprising:
  - (a) preparing a powdered admixture of the refractory particles and metallic alloy;
  - (b) subjecting said admixture to sufficient heat and pressure to produce an integral, sintered compact;
  - (c) cooling said compact; and
  - (d) subjecting said compact to high applied stress to include formation of martensite in the surface layer of said composite.

#### Patentansprüche

1. Gebundene Carbidmischung, enthaltend feuerfeste Teilchen, enthaltend Wolframcarbid und gegebenenfalls Zusätze von Titancarbid, Tantalcarbid und/oder anderen feuerfesten Materialien innerhalb einer metallischen Bindemittelgrundmasse, worin die Grundmasse zwischen 3 und 20 Gewichtsprozent der Mischung ausmacht und aus zwischen 5 und 50% Nickel, einer Menge von bis zu 2% Kohlenstoff, ausreichend zur Vermeidung der Bildung eines schädlichen Kohlenstoffmangels oder von Überschußphasen und, abgesehen von Verunreinigungen, einem aus Eisen bestehenden Rest, besteht.
2. Gebundene Carbidmischung, enthaltend feuerfeste Teilchen, enthaltend Wolframcarbid und gegebenenfalls Zusätze von Titancarbid, Tantalcarbid und/oder anderen feuerfesten Materialien innerhalb einer metallischen Bindemittelgrundmasse, worin die Grundmasse zwischen 3 und 20 Gewichtsprozent der Mischung ausmacht und aus zwischen 5 bis etwa 30% Nickel, 5 bis 20% Mangan, einer Menge von bis zu 2% Kohlenstoff, ausreichend zur Vermeidung der Bildung eines schädlichen Kohlenstoffmangels oder von Überschußphasen und, abgesehen von Verunreinigungen, einem aus Eisen bestehenden Rest, besteht.
3. Mischung nach einem der Ansprüche 1 oder 2, dadurch gekennzeichnet, daß die Mischung eine austenitische Grundmasse aufweist, die sich an der Oberfläche bei angewandter Beanspruchung partiell in Martensit umwandelt.
4. Verfahren zum Bohren durch Gestein mit einem Werkzeug aus gebundenem Carbid, dadurch gekennzeichnet, daß das Werkzeug aus der gebundenen Carbidmischung gemäß irgendeinem der vorhergehenden Ansprüche besteht.
5. Verfahren zur Herstellung der Mischung gemäß irgendeinem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß man
  - (a) eine gepulverte Mischung der feuerfesten Teilchen und der metallischen Legierung herstellt,
  - (b) die Mischung zur Herstellung eines integralen, gesinterten Preßlings ausreichend erwärmt und unter Druck setzt,
  - (c) den Preßling kühlt, und
  - (d) den Preßling einer hohen angewandten Beanspruchung unterwirft, um die Bildung von Martensit in der Oberflächenschicht der Mischung einzuschließen.

#### Revendications

1. Composé cimenté comportant des particules réfractaires comprenant du carbure de tungstène et en option une addition de carbure de titane, de carbure de tantale et/ou d'autres réfractaires à l'intérieur d'un liant pour matrice métallique, dans lequel la matrice représente entre 3 et 20% en poids du composé et comporte entre 5 et 50% de nickel, une quantité allant jusqu'à 2% de carbone suffisante pour éviter la formation de phase déficiente en carbone ou ayant un excès de carbone nuisible et le complément étant constitué par du fer à l'exception des impuretés.
2. Composé cimenté comportant des particules réfractaires comprenant du carbure de tungstène et en option des additions de carbure de titane, carbure de tantale et/ou autres réfractaires à l'intérieur d'un liant pour matrice métallique, dans lequel la matrice représente entre 3 et 20% en poids du composé et comprend entre environ 5 et 30% de nickel, 5 et 20% de manganèse, une quantité allant jusqu'à 2% de carbone suffisante pour éviter la formation de phase déficiente en carbone ou ayant un excès de carbone nuisible et le complément étant constitué par du fer indépendamment des impuretés.
3. Composé selon l'une quelconque des revendications 1 ou 2 dans laquelle le composé a une matrice austénitique qui se transforme partiellement en martensite à la surface sous contrainte appliquée.
4. Procédé de forage de roche avec un outil en carbure cimenté caractérisé en ce que l'outil est constitué par le composé de carbure cimenté selon l'une quelconque des revendications précédentes.
5. Procédé de production du composé selon l'une quelconque des revendications 1 à 3 caractérisé en ce qu'il consiste à:

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- (a) préparer un mélange en poudre des particules réfractaires et de l'alliage métallique;
- (b) soumettre ce mélange à une température et une pression suffisante pour produire un comprimé compact fritté;
- (c) refroidir ce comprimé; et
- (d) soumettre ce comprimé à une contrainte appliquée élevée pour former de la martensite dans la couche superficielle du composé.

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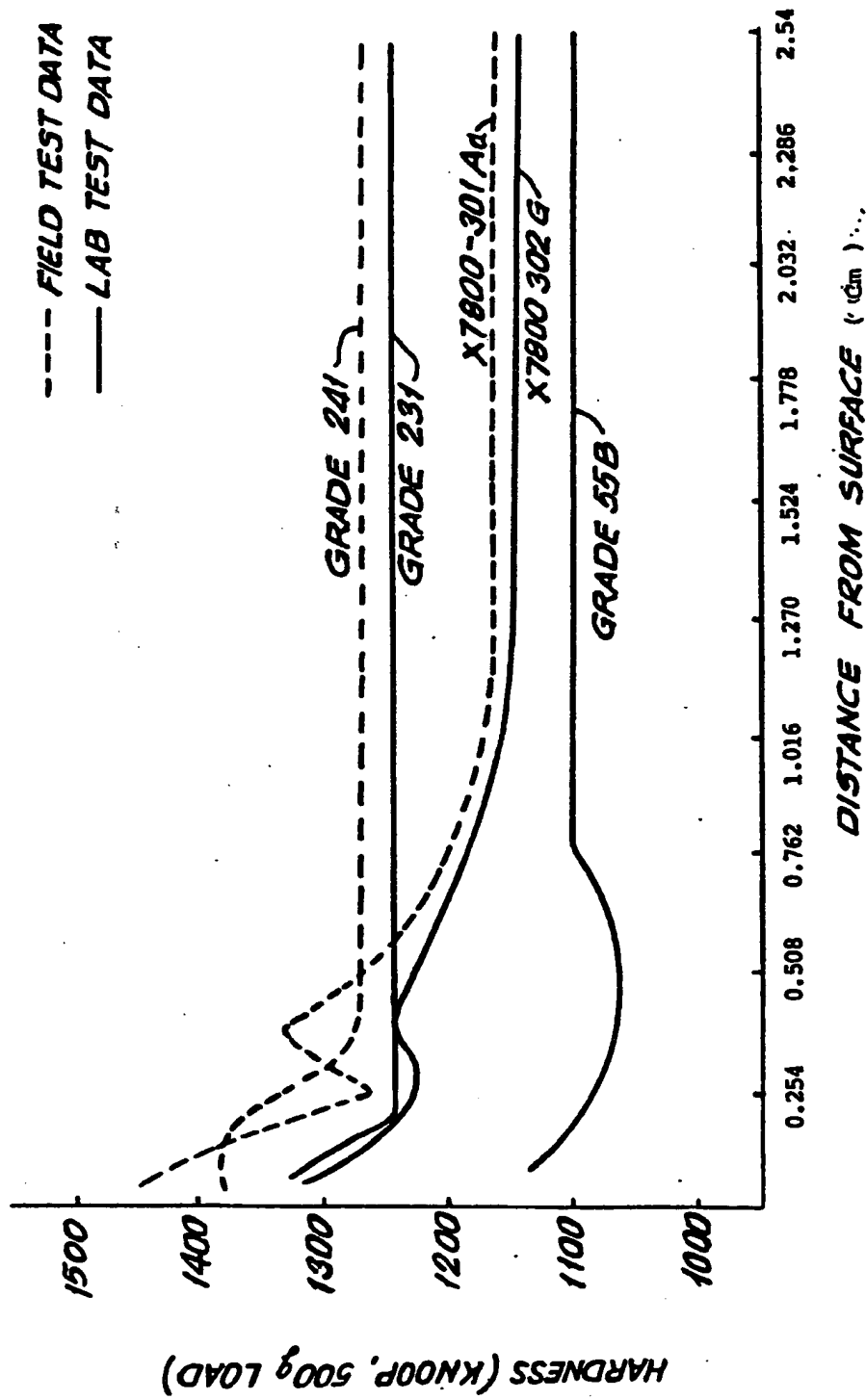


FIG. 1

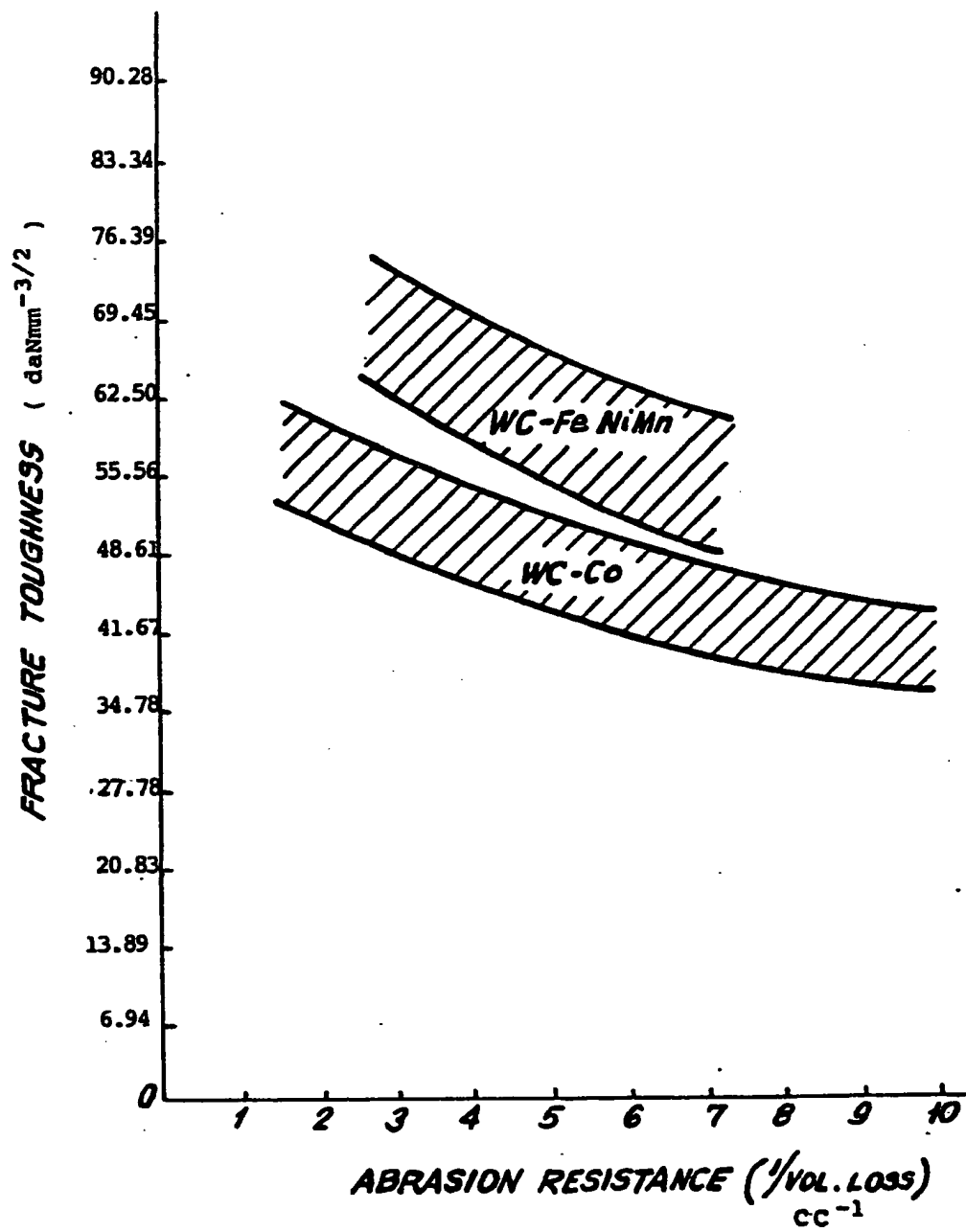


FIG.2